FINAL TECHNICAL REPORT OF GRANT N00014-93-1-G037

Title: *Measurements of Ultraviolet Absorption Cross Sections of NO_2 at Various Pressures and Temperatures*
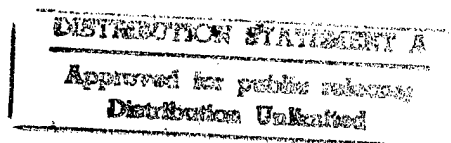
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Abstract

Laboratory measurements of the absoprtion cross sections of NO_2 at the temperature 298.5 K have been made throughout the wavelength region 360 nm to 470 nm. The equilibrium constant K_p has been experimentally obtained as 150 hPa, from which the column density of pure NO_2 is obtained. The cross sections almost completely agree with the recent results of Mérienne *et al.* [J. Atmos. Chem. 20, 281-297 (1995)]. The cross sections at the higher resolution of 0.14 cm^{-1} have been obtained in the wavelength region where the spectra have fine structure.

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1   Introduction

NO_2 plays a critical role in stratospheric ozone chemistry. The nitrogen oxides, NO and NO_2, are introduced into the atmosphere by the reaction of N_2O, which is naturally produced by bacterial action on organic material in the ground. NO_2, produced at the surface, diffuses upwards into the atmosphere, where, in collision with atomic oxygen, NO is formed. NO in reaction with ozone is rapidly converted to nitrogen dioxide. The photodissociation of NO_2 and its increasing presence as an atmospheric pollutant, combine to make it an important participant in the chemistry of the lower atmosphere.

Knowledge of the absorption cross section of NO_2 is requires in order to interpret measurements, and for calculation of the rate coefficient for NO_2 photodissociation in the atmosphere.

The electronic absorption spectrum of NO_2 is known to extend from 320 to 1000 nm. The spectrum consists of a very large number of bands, and there is no obvious regularity either in the vibrational structure or in the rotational structure of the individual bands. The analysis of these bands has been a long-standing spectroscopic problem which is still largely unsolved. Douglas and Huber [1965] investigated the six absorption bands of $^{14}NO_2$ and $^{15}NO_2$ in the region 370 -460 nm, and assigned them to $K_a = 0 \leftarrow 1$ subbands of the electronic transition $^2B_1 \leftarrow^2 A_1$.

In preparation for photoelectric measurements of the absolute ultra violet absorption cross section of NO_2, we borrowed the high resolution, photographic plates of NO_2 absorption by Douglas and Huber [1965] and studied what wavelength resolution was necessary for the cross section measurements of NO_2. We had planned to use these spectra for wavelengths calibration of our cross section measurements, but abandoned the plan because of the lack of isolated sharp lines in the bands.

2   Experimental Procedure

We used the 6.65-m, normal incidence, vacuum spectrometer in the first order of a 1200 l/mm grating to obtain photoabsorption cross section measurements of NO_2. The grating was blazed at 5500 Å, and provided an estimated instrumental width of 0.0025 nm with entrance and exit slit widths of 0.010 mm. The stainless steel absorption cell was connected directly to the entrance slit assembly of the spectrometer and was closed with two fused silica windows (Fig. 1). The path length was 42.3 cm. The continuous background for the photoabsorption measurements was provided by a tungsten lamp operated on 12 V ac. The NO_2 gas (Matheson, 99.5%) was purified

by the method of fractional distillation, and was kept in a liquid-nitrogen cooled trap. The NO_2 was warmed up slowly and introduced into the absorption cell. NO_2 pressures of 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 Torr were used and measured with a capacitance manometer (MKS Baratron, 10 Torr).

Slit Chamber   Mirror

Absorption Cell   Lens   Hollow Cathode Lamp (Fe-Ne)
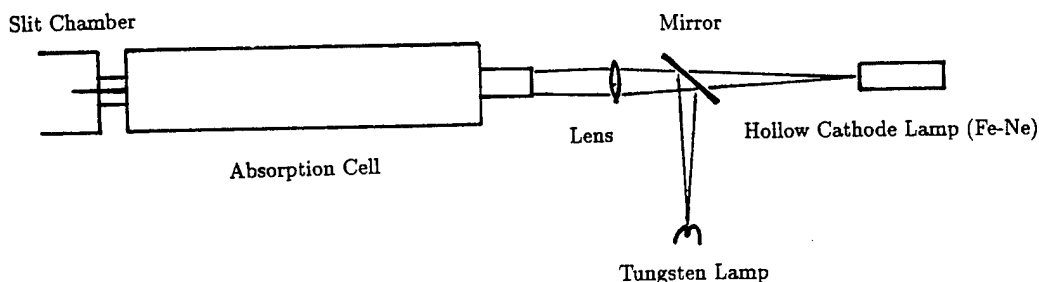
Tungsten Lamp

Figure 1: Experimental arrangement of absoprtion cell, background continuum source, and hollow cathode lamp.

We divided the spectral region (360 nm - 470 nm) into sixteen sections of about 7.5 nm extent. The background continuum level was established by scanning the empty cell before and after each photoabsorption measurements, and comparing with the background intensity levels without NO_2 in the cell. We obtained data points every 0.0015 nm at a resolution of 0.0040 nm. The cross section measurements for the most structured region were also obtained with a resolution of 0.0025 nm for every 0.0003 nm step. In each scan range, two extra scans were obtained; the back ground scan without any NO_2 in the cell and the scan of the hollow cathode lamp (Fe/Ne, 20 mA) for wavelength calibration. Some times we also took a scan of both the main NO_2 spectrum and the hollow cathode spectrum to avoid any systematic shift in wavelength. The wavelengths of Fe I, Fe II, and Ne I lines are well known ($\pm$ 0.001 Å). The uncertainty of the wavelength calibration depended on the scan step, which was 0.015 Å and for the high resolution scan, 0.003 Å.

Most of the uncertainty in cross section measurements with a single beam spectrometer is in the estimation of the background intensity levels since they vary with time and wavelength during photoabsorption scan. It is also difficult to keep the column density of NO_2 constant in the absorption cell during the scan. To overcome these problems, we measured the cross section at the very beginning of every scan when the NO_2 gas was fresh, and the background, I_0, was well known. We obtained these absolute points for sixteen wavelengths and six pressures. The observed cross

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sections are a linear function of pressure, and therefore a linear extrapolation to zero pressure provides the cross sections of pure NO_2. The resulting cross sections at zero pressure, σ_0, are given in Table I along with slopes. The cross sections (σ_0) can be used as the absolute cross sections. The ratio of the observed to absolute cross sections gives the fraction of NO_2 density at that pressure, and these are given in Table 2 for fourteen runs. The averaged fractions are given in the same table with the uncertainties (1σ and $\sigma/\sqrt{n}$), and are also plotted in Fig. 2. The equilibrium constants K_p are given by

$$K_p = \frac{p^2(NO_2)}{p(N_2O_4)}. \tag{1}$$

The dotted curves in the figure are the fractions vs. pressures calculated from values of K_p with the curves in order from the top, K_p of 160, 150, and 140hPa. Our observed fractions agree very well with the fraction calculated with $K_p = 150$. Hurtmans et al. [1993] determined the K_p value by fitting the literature values with a fourth degree polynomial expansion in the temperature. According to Roscoe and Hind [1993], the error in the literature values of the equilibrium constants is about 5%, but we could estimate the constants with an uncertainty of better than 2%.
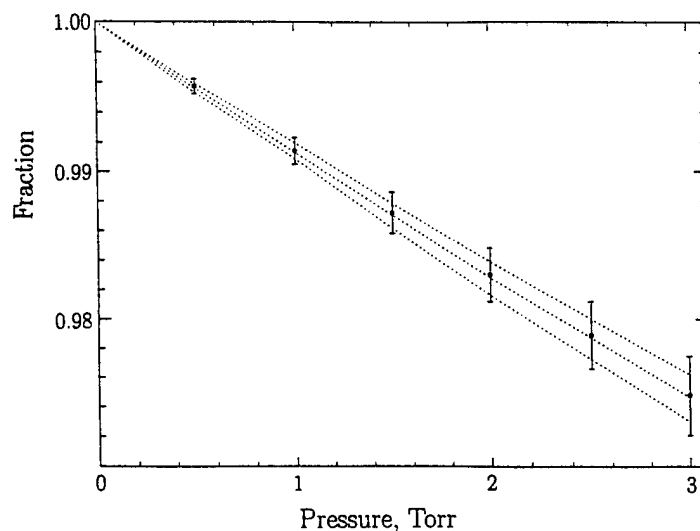

Figure 2: The observed fractions of NO_2 plotted against the total pressure. The dotted curves are calculated fractions of NO_2 with $K_p = 160$, 150, and 140 (in the order from the top). The observation agree with $K_p = 150$, which is expected for a temperature of 298.54 K.

Table 1. Cross Sections of NO_2 at 295 K and pressure dependencies.

Run	Wavenumber cm^{-1}	Wavelength nm(air)	σ_0 10^{-19}cm^2	Slope 10^{-19}cm^2/Torr
R35	27824.74	359.2899	4.56± 0.20	0.0306
R36	27242.44	366.9698	5.29± 0.18	-0.0206
R37	26685.10	374.6345	5.19± 0.05	-0.0381
R38	26137.12	382.4891	5.44± 0.05	-0.0285
R39	25599.86	390.5165	6.17± 0.06	-0.0619
R40	25164.98	397.2652	5.56± 0.03	-0.0706
R41	24744.51	404.0159	6.38± 0.05	-0.0783
R42	24346.00	410.6289	6.82± 0.02	-0.0283
R43	23953.98	417.3496	5.54± 0.03	-0.0480
R44	23576.06	424.0398	6.34± 0.08	-0.1203
R45	23218.81	430.5641	6.10± 0.04	-0.0609
R46	22864.07	437.2446	4.31± 0.03	-0.0614
R47	22521.29	443.8997	4.44± 0.02	-0.0548
R48	22244.90	449.4152	4.31± 0.08	-0.0376
R49	21873.73	457.0414	3.83± 0.02	-0.0358
R50	21533.08	464.2717	4.15± 0.03	-0.0102

Table 2. Fractions of NO_2 density versus pressure

P(NO_2), Torr	0.5	1.0	1.5	2.0	2.5	3.0
R36	0.9981	0.9961	0.9942	0.9923	0.9904	0.9885
R37	0.9963	0.9927	0.9891	0.9855	0.9820	0.9784
R38	0.9974	0.9948	0.9922	0.9896	0.9871	0.9845
R39	0.9950	0.9901	0.9852	0.9803	0.9755	0.9708
R40	0.9937	0.9875	0.9813	0.9752	0.9692	0.9633
R41	0.9939	0.9879	0.9819	0.9760	0.9702	0.9645
R42	0.9979	0.9959	0.9938	0.9918	0.9897	0.9877
R43	0.9957	0.9914	0.9872	0.9830	0.9788	0.9747
R45	0.9950	0.9901	0.9852	0.9804	0.9756	0.9709
R46	0.9929	0.9860	0.9791	0.9723	0.9656	0.9590
R47	0.9939	0.9878	0.9818	0.9759	0.9701	0.9643
R48	0.9957	0.9913	0.9871	0.9828	0.9786	0.9745
R49	0.9954	0.9908	0.9862	0.9817	0.9772	0.9728
R50	0.9988	0.9975	0.9963	0.9951	0.9939	0.9927
Average	0.9957	0.9914	0.9872	0.9830	0.9789	0.9748
σ	0.0017	0.0034	0.0051	0.0068	0.0085	0.0101
$\sigma/\sqrt{n}$	0.0005	0.0009	0.0014	0.0018	0.0023	0.0027

3   The cross sections of NO$_2$

The cross sections of every scan were obtained by the Beer-Lambert law assuming
that the observed pressure represents the pure NO$_2$ concentration, and later were
calibrated to the true cross sections by using the fractions of NO$_2$ density shown in
Table 2. The cross sections at the beginning of the scan presented in Table 1 are
the absolute cross sections because the column densities are obtained with a fresh
NO$_2$ sample. The cross sections at the end of scan are calibrated with the beginning
value of the following scan of the next wavelength region with the same pressure. All
cross sections obtained with different pressures are put together to reduce the final
cross sections of the each sections. However data with optical depths higher than
2.0 and lower than 0.30 are omitted from summations. Our final cross sections are
presented in Fig. 3 for the wavelength region 360 to 470 nm. These cross sections
agree so well with the recent measurements by Mérienne et al. [1995], that there are
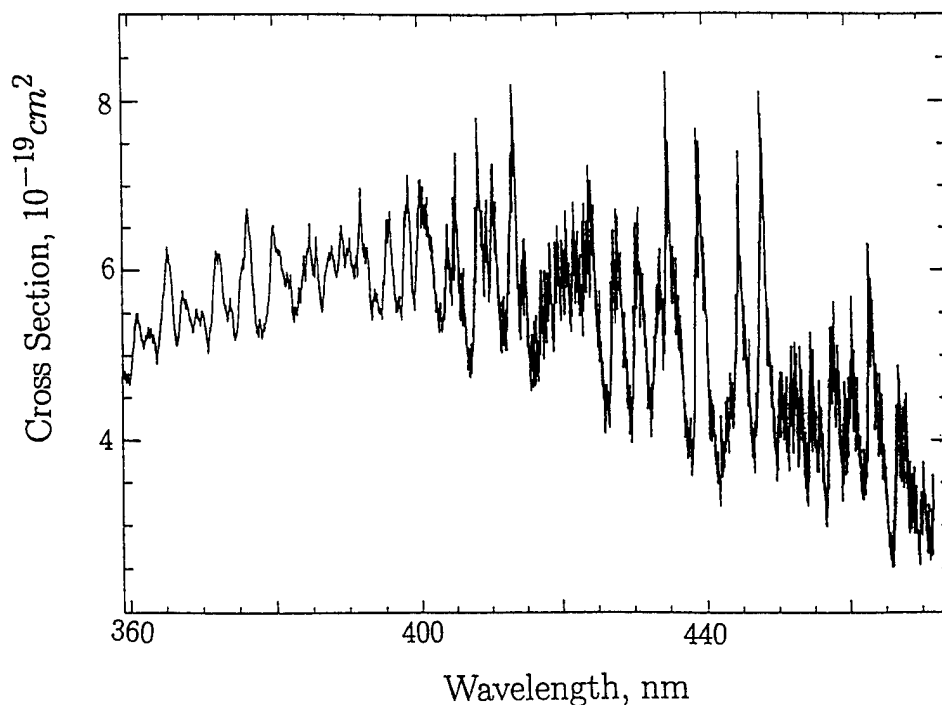no measurable differences on this scale.

Figure 3: The absorption cross sections of NO$_2$ at 298.5 K in the wavelength region
360 to 470 nm (air).

Table 3. Wavelength Region of High Resolution Cross Sections

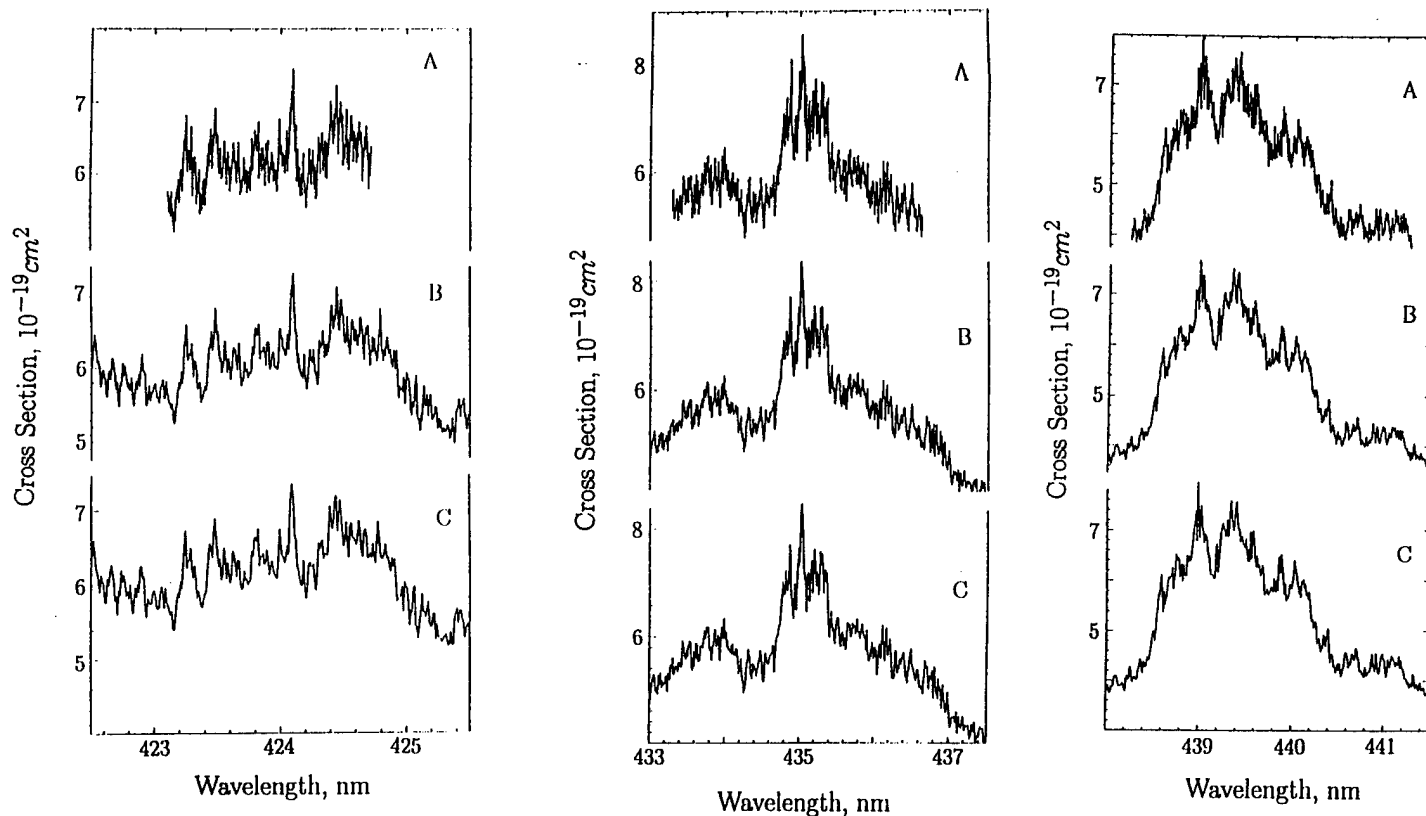| File	Wavelength Region, nm	
	begining	end
411	404.8	407.2
412/3	407.7	410.8
421/2	412.4	415.5
431	423.2	424.8
441	426.9	428.6
451	430.1	431.5
452/3	433.4	436.8
461/2	438.3	441.4
471	444.0	445.7
472	447.3	449.1
481	454.3	455.7
482	451.7	453.1
491	462.7	464.1

Figure 4: (A): The absorption cross sections of NO_2 at the high resolution of 0.14 cm^{-1}. (B): the cross sections at the resolution of 0.28 cm^{-1}. (C) The cross sections of Mérienne et $al.$ [1995] at the resolution of 0.50 cm^{-1}.

The cross section measurements at high resolution covered several wavelength region, where the fine band structures are observed. The high resolution scan used the instrumental width of 0.0025 nm, and data points were taken every 0.003 nm step. The wavelength region for the high resolution scan are tabulated in Table 3. A few examples of the high resolution scan are presented in Fig. 4 through 6 for wavelength region of around 424, 435, and 440 nm. The figures also show our regular scans and those of Mérienne et al. [1995] for comparison. Except in the details, there are almost no differences among the three scans.

The three recent independent measurements of NO_2 cross sections [Mérienne et al., 1995; Vandaele et al., 1996; and ours] in the wavelength region 370-470 nm agree very well. The three groups are planing to combine all these recent data to obtain the recommended cross sections of NO_2 for the convenience of application in atmospheric studies. The cross sections reported here are available at a wavelength interval of 0.005 nm on the World Wide Web. The URL is http://cfa-www.harvard.edu/amp/data/amdata.html.

The cross sections of NO_2 mixed with air and nitrogen gas, were also measured at the same conditions. The values of the cross sections of NO_2 mixed with nitrogen are more or less the same as those of the pure NO_2 gas. However, the cross sections measurements of NO_2 mixed with air lead to very low values compared with those of the pure gas. The re-analysis of the mixed gases composition could not explain why smaller cross sections were observed with NO_2 in the air. We also measured the cross section of NO_2 at 225 K, but it will take more time for the data analysis because the analysis must include consideration of the dimer population.

ACKNOWLEDGMENTS

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